Particuology xxx (2014) xxx–xxx

Contents lists available at ScienceDirect

Particuology

journal homepage: www.elsevier.com/locate/partic

Direct transformation of FGD gypsum to calcium sulfate hemihydrate whiskers: Preparation, simulations, and process analysis

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ARTICLE INFO

Article history:
Received 7 March 2014
Received in revised form 26 March 2014
Accepted 3 April 2014

Keywords:
FGD gypsum
Calcium sulfate
Whisker
Direct transformation
Simulation analysis

ABSTRACT

Calcium sulfate hemihydrate (CSH) whiskers were synthesized by phase transition in $CaCl_2$ solution under atmospheric pressure. Analytical-grade calcium sulfate dihydrate (AR CSD) was used as the raw material for the synthesis of CSH whiskers, according to orthogonal experiments. The effects of reaction temperature, AR CSD content, H_2SO_4 content, and reaction time were investigated, and the crystallization conditions were optimized. The as-prepared CSH whiskers displayed a regular morphology and a highly uniform size, with an aspect ratio of 105. A simulation system was also established by blending various sulfates with AR CSD, to evaluate the effects of impurities in flue gas desulfurization (FGD) gypsum. The main aim was to prepare CSH whiskers directly from FGD gypsum, without any purification, using the optimized conditions. This is a facile potential alternative process for large-scale production of CSH whiskers using abundant FGD gypsum as source materials.

Introduction

Flue gas desulfurization (FGD) processes using calcium-based absorbents have been very successful in the removal of sulfur dioxide, and are used in over 90% of coal-fired power plants (Guan et al., 2011b; Kairies, Schroeder, & Cardone, 2006). However, there are environmental concerns regarding the large amounts of FGD gypsum produced during FGD processes, up to 50 million tons per year since 2009, as this significantly increases the risk of chemical contamination by sulfite-rich FGD scrubber sludge generated by landfill disposal (Guan et al., 2011a). Suitable uses for FGD gypsum (which consists mainly of calcium sulfate dihydrate, CSD) urgently need to be found, such as setting retarders in cement (Chandara, Azizli, Ahmad, & Sakai, 2009; Tzouvalas, Rantis, & Tsimas, 2004), road sub-bases for construction (Hua et al., 2010), and concrete block manufacture (Leiva et al., 2010; Yazici, 2007). Increasing attention is being paid to high-value-added transformations of FGD gypsum to obtain more profitable products. Calcium sulfate hemihydrate (CSH) whiskers, fiber-shaped single crystals with large length-to-diameter ratios, have low solubility, good thermal stability, superior workability, high strength, and good compatibility; they have potential applications as fillers or reinforcing agents in building (Guan et al., 2011a), medicine (McConville, Ross, Florence, & Stevens, 2005), and papermaking (Hamdona & Al Hadad, 2007).

Much effort has been made to control the crystallization and morphology of CSH whiskers to improve their performance and extend their applications (Luo, Li, Xiang, Li, & Ning, 2010). Bivalent salt solutions containing Ca^{2+} and ${SO_4}^{2-}$ are usually used as the precursor solution, and CSH whiskers have traditionally been synthesized hydrothermally in an autoclave at temperatures above 100 °C, with high steam partial pressures (Duda & Koslowski, 1991; Feldmann & Demopoulos, 2012b; Xu, Li, Luo, & Xiang, 2011). In recent decades, organic agents have been used in CSH preparation, for structure enhancement. Song, Sun, Fan, and Yu (2003) used bis(ethylhexyl) hydrogen phosphate as a Ca^{2+} extractant to control the CSH size and morphology. Kong, Yu, Savino, Zhu, and Guan (2012) designed a water/*n*-hexanol/cetyltrimethylammonium bromide reverse microemulsion for preparing CSH. Another promising process for the synthesis of CSH by direct transformation using CSD as the precursor has been suggested. Mixed boiling or near-boiling solutions of inorganic acids and their salts (Guan et al., 2009, 2011a, 2011b) are generally used as the crystallization medium.

In this study, a direct phase-transition method using a salt solution was used for the preparation of CSH whiskers. Processes performed at low temperature and ambient pressure are more energy efficient than autoclave methods. Analytical-grade calcium sulfate dihydrate (AR CSD) was used as an analog of FGD gypsum to

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http://dx.doi.org/10.1016/j.partic.2014.04.010
1674-2001/© 2014 Published by Elsevier B.V. on behalf of Chinese Society of Particuology and Institute of Process Engineering, Chinese Academy of Sciences.

determine the optimum preparation conditions, i.e., reaction temperature, CSD content, reagent concentration, and reaction time. Several sulfates were added to the AR CSD, simulating the main impurities in FGD gypsum, to determine the effects of impurities. The objective was to develop a one-pot direct synthesis of CSH whiskers using FGD gypsum under the optimized conditions.

Experimental

Materials

FGD gypsum (Shanghai Waigaoqiao No. 3 Power Generation Co., Ltd., China) and AR CSD (Sinopharm Chemical Reagent Co., Ltd., China) were used as the raw materials. All other reagents used in the study were obtained from the Sinopharm Chemical Reagent Co., Ltd., and used without further purification.

Preparation procedure

$CaCl_2$ (5, w/v%) solution was placed in a three-necked flask and heated at the required reaction temperature. The following reagents were then added, in sequence, to produce a suspension: a given amount of H_2SO_4 solution, AR CSD or FGD gypsum, and oleic acid (0.005, w/v%). The slurry was heated and stirred at a speed of 800 rpm. Samples were removed at different times. The reaction was terminated when white floccules were observed. The as-prepared products were immediately filtered, washed with boiling distilled water, and dried at 80 °C for 3 h. To demonstrate the effects of impurities in FGD gypsum, appropriate amounts of $MgSO_4$, $Al_2(SO_4)_3$, or $Fe_2(SO_4)_3$ were added to the slurry; the samples are denoted by CS–X, where X is $MgSO_4$, $Al_2(SO_4)_3$, or $Fe_2(SO_4)_3$.

Characterization

The morphologies and surface compositions were determined using scanning electron microscopy/energy-dispersive X-ray spectroscopy (SEM/EDX; JSM-6700F; JEOL). The phase composition was examined by X-ray diffraction (XRD), using a D/max-2500 diffractometer, with Ni-filtered Cu Kα radiation (V = 50 kV, I = 80 mA) at a scanning rate of 8°/min. The crystal morphologies of the CSH whiskers were examined using an optical microscope (DM2500M;

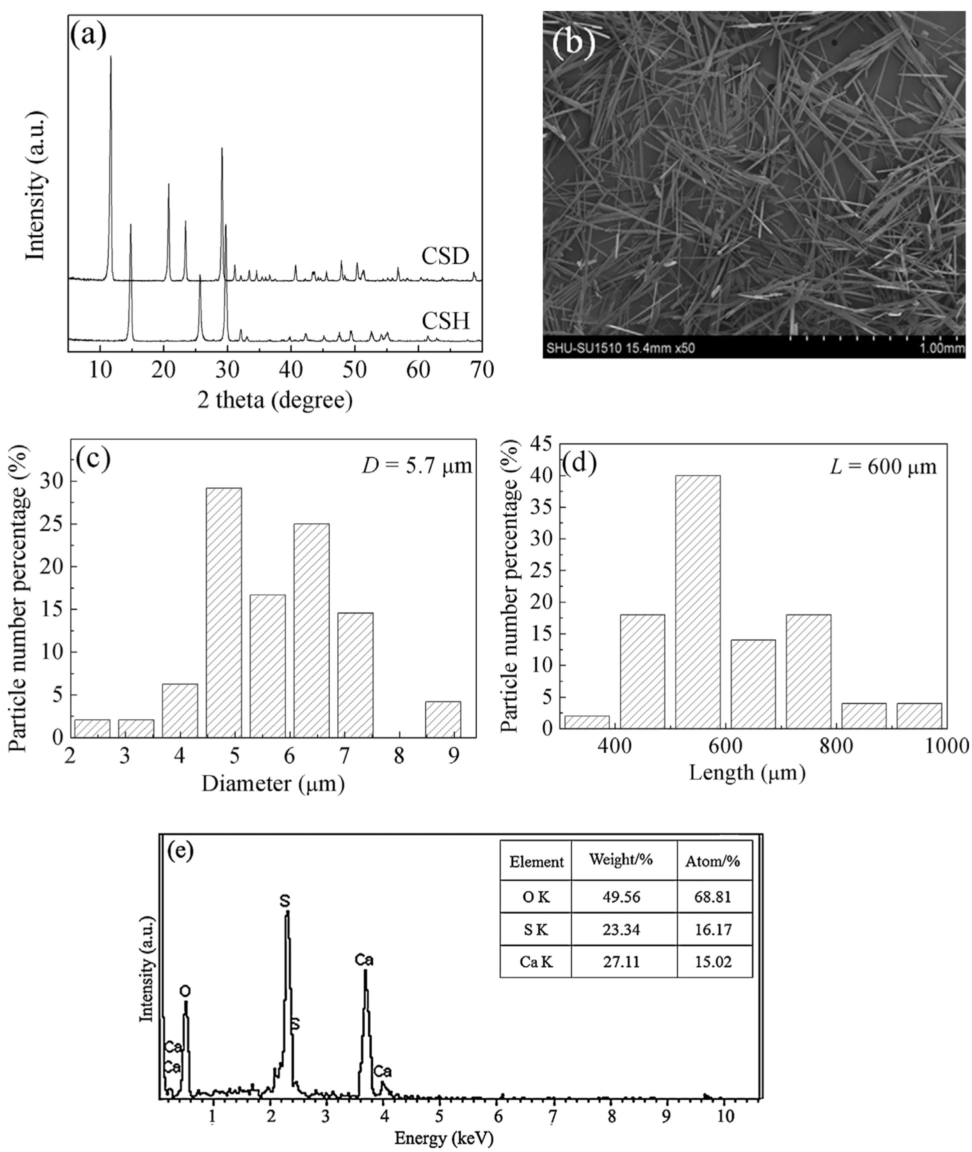

Fig. 1. XRD diffraction patterns (a); SEM image (b); particle diameter (c) and length (d) distributions; and EDX spectrum and its elemental composition (e) of CSH whiskers obtained under the optimum conditions.

Please cite this article in press as: Miao, M., et al. Direct transformation of FGD gypsum to calcium sulfate hemihydrate whiskers: Preparation, simulations, and process analysis. *Particuology* (2014), http://dx.doi.org/10.1016/j.partic.2014.04.010